Water chemistry on Rutile(110) at near-ambient conditions

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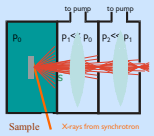
Photoemission at near-ambient pressures

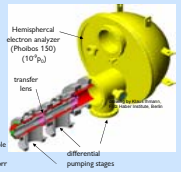
Fundamental limit in High-pressure XPS :

Elastic and inelastic scattering of electrons by gas molecules.

Solution: differential pumping and electrostatic lens system

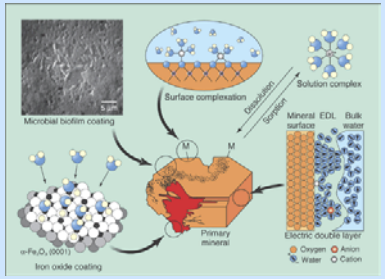


ALS beamline 11.0.2 high-pressure PES



D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, Rev. Sci. Instrum. 73 (2002) 3872.

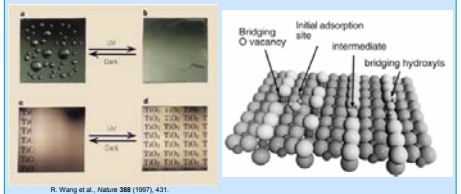
Water on mineral surfaces



Reactions at interfaces are strongly influenced by the structure and chemical composition of the interface.

Water on TiO_2

- TiO_2 is hydrophobic in darkness
- TiO_2 becomes hydrophilic upon UV-irradiation
- defects are believed to play an important role for the hydrophilicity of titania

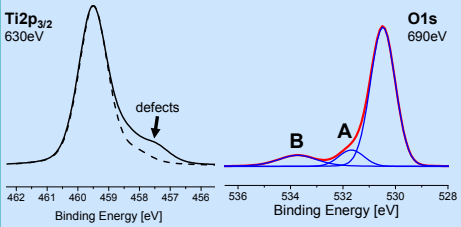


R. Wang et al., *Nature* **388** (1997), 431.

Defects on TiO_2(110) react rapidly with water

Sputtering introduces surface defects (solid line) that are immediately healed when the surface is exposed to water >0.1 mTorr (dashed line)

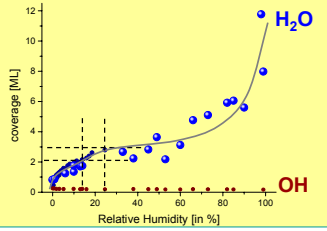
Exposure to water leads to bridging OH (A) and molecular water (B)



TiO_2(110)

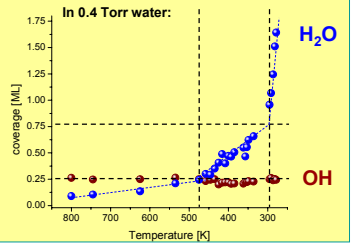
Isobars at different pressures

The OH concentration saturates at 0.25 ML. The plot shows the water coverage as a function of relative humidity.



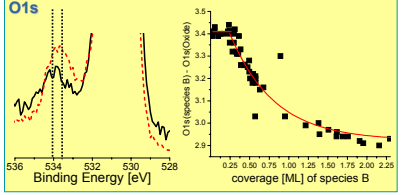
Water isobar

The adsorption isobar of water shows kinks at a coverage of 0.25 ML and 0.75 ML due to particularly stable structures.



Two types of water

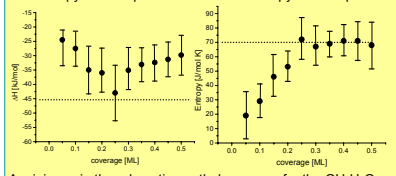
0.25 ML water are stabilized due to strong charge transfer to the surface OH groups (hydrogen bonding). For higher coverage, charge transfer becomes less important and we observe an O1s peak shift to lower binding energy (-0.5 eV).



Isosteric evaluation of isobars

A plot of lnp vs. 1/T for constant coverage gives

enthalpy of adsorption and entropy of adsorption.

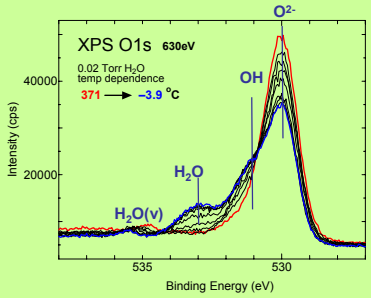


A minimum in the adsorption enthalpy occurs for the OH-H_2O species at 0.25 ML coverage. For higher coverage, the entropy approaches the value of liquid water.

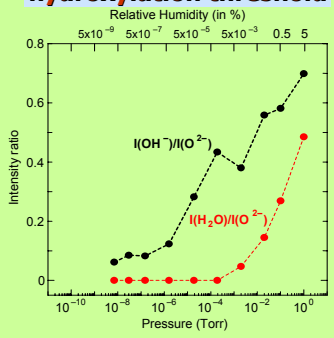
Fe_2O_3(0001)

Water isobar

Temperature dependence at p(H_2O)= 0.02 Torr



Water isotherm: hydroxylation threshold



Summary

- Water adsorption on TiO_2(110) and Fe_2O_3(0001) follow different adsorption mechanisms
- On TiO_2(110), defects react rapidly to form 0.25 ML OH at bridging sites. 0.25 ML water binds strongly to OH, further water adsorption occurred on Ti sites close to these nucleation sites.
- On Fe_2O_3(0001), the hydroxylation threshold is >10^{-6} Torr water. Water adsorption starts after partial hydroxylation. The surface gets completely hydroxylated and water binds to the OH-terminated surface.

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